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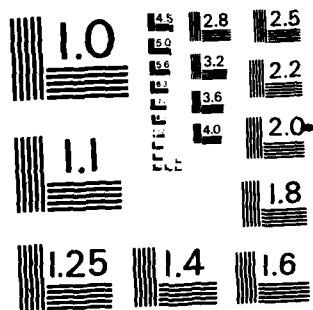   D K BOWEN ET AL. NOV 83 DL/SCI/P399E N00014-83-K-0468   1/1

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TOPOGRAPHIC EXAFS

by

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13. ABSTRACT

Contrast near an absorption edge has been observed in synchrotron radiation topographs obtained with white radiation due to the variation of wavelenth across an image. Variations in absorption, due to the fluctuations in the EXAFS spectrum, appear as fringes parallel to the edge. The contrast has been measured densitometrically for a Nb specimen and excellent agreement obtained with a conventional EXAFS spectrum. The exposure time for the topograph was 25 s. The spectral characteristics of this technique are analysed and shown to be comparable with standard EXAFS spectroscopy. The method provides a means of extracting microstructural and spectroscopic information simultaneously and point-by-point on one sample. Possible applications are discussed.

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Topographic EXAFS

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Abstract

Contrast near an absorption edge has been observed in synchrotron radiation topographs obtained with white radiation due to the variation of wavelength across an image. Variations in absorption, due to the fluctuations in the EXAFS spectrum, appear as fringes parallel to the edge. The contrast has been measured densitometrically for a Nb specimen and excellent agreement obtained with a conventional EXAFS spectrum. The exposure time for the topograph was 25 s. The spectral characteristics of this technique are analysed and shown to be comparable with standard EXAFS spectroscopy. The method provides a means of extracting microstructural and spectroscopic information simultaneously and point-by-point on one sample. Possible applications are discussed.

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The EXAFS method of absorption-edge spectroscopy for the determination of crystal bond lengths and coordination number, especially in the first coordination shell, was invented in 1920[1] and is in very widespread use in chemical, crystallographic, biological and to some extent metallurgical research. The high-resolution method of x-ray diffraction topography, which reveals crystal defects, was invented in 1959[2] and is likewise widely used in studies on crystal growth, phase transformations, chemical decomposition and mechanical properties and domain studies: that is, in the area of 'microstructure' rather than 'crystal structure'. It is obvious that the techniques are complementary and that both could be required to solve a particular problem - structural changes induced by segregation at a surface or internal interface, for example. However, up to now, EXAFS data have been taken only as an average over large samples, thus losing all microstructural information, and topographic data have not provided structural, bonding or chemical information. This paper presents the first experimental method of combining these experiments, simultaneously on one specimen.

The method relies upon the properties of synchrotron radiation (SR), which has enabled both EXAFS and X-ray topographic methods independently to make major advances in the study of materials and other systems[3]. The high intensity and continuous spectrum of SR enables EXAFS spectra to be accumulated in reasonable times (some tens of minutes) and X-ray topographs to be taken in some seconds. An obvious way of combining the methods would be to take an X-ray topograph to locate areas of interest, place an aperture of diameter equal to the resolution required in this area and measure successive EXAFS spectra during a linear or raster scan of the area. This method would certainly provide the best spectral data, but a rapid calculation of available intensities shows that with most current SR

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sources the data collection times would be quite impractical - days or weeks. It would be worth performing this experiment on the very high intensity beams available from wiggler magnets, but these are rather scarce in the world.

A possibility for speeding up the spectral data collection is the use of white radiation incident upon the sample, followed by a dispersing element (e.g. bent crystal) and a film or linear detector; this has recently been achieved[4,5] and results in dramatic decreases in data collection times. The topographic data can then be collected in a separate exposure.

If a good quality single crystal is being used as the specimen, as it often is when topographic information is sought, then there is a further and very simple technique: use the specimen as its own monochromator. In the white radiation topographic method (Fig.1), the incident beam diverges from the SR source, which is some tens of metres distant from the specimen. There is therefore a small variation of incident Bragg angle across a specimen, and a consequent variation of wavelength (energy) selected by the specimen for diffraction. There is a fortunate coincidence, in that the energy resolution and range for a typical SR source and specimen geometry is often well matched to the spectral requirements for EXAFS.

The experimental procedure is as follows. The orientation of the specimen is chosen and set so that the wavelength selected by some part of the specimen is at the absorption edge under study. A television image converter is extremely useful for this setting as the absorption edge is easily visible: in fact, the results reported here were obtained in the course of setting up for a quite different experiment for which a wavelength just beyond the edge was required. A standard topographic image is then recorded on high resolution plate, e.g. Ilford nuclear emulsion L4,

exposed so that the high absorption side of the image is in good contrast. The wavelength selected by a point on the image is a direct function of the distance on the image from the edge, measured normally to the latter. The diffracted beam falling on each point will therefore have suffered absorption characteristic of a given energy on the absorption spectrum. This results in 'fringes' in the image, parallel to the image of the edge, corresponding to maxima and minima in the EXAFS spectrum.

Experimental results

The first results, taken on the white radiation camera[6] at the SRS, Daresbury Laboratory, are shown in Figs.2-5. Figure 2 shows the standard topographic image of a 125 μm thick Nb specimen at the Nb Kα edge, reproduced photographically. The absorption edge is clear, but the fringes have weak contrast (about on the limit of the contrast sensitivity of the human eye!) and are not evident. However, image processing techniques can be used to reveal them. The original plate was digitised on a Joyce Loebl flat bed densitometer with 5 μm resolution and the resulting matrix digitally smoothed and processed to cut off low and high values and to stretch the contrast. The result is shown in Fig.3; Fig.4 shows a differentiated version of Fig.3. In each of these, especially the latter, the fringes are easily visible. Figures 5a and 5b show density variations along the lines marked AA and BB in Fig.3. These show, albeit noisily, typical EXAFS spectra.

In order to demonstrate that these are indeed EXAFS-type data, comparison was made with an EXAFS spectrum taken on a rotating-anode generator of a 25μm thick Nb foil, Fig.6. A rotating anode generator with a Mo target and a Si 800 bent crystal monochromator were used. The spectra in Figs.5 and 6 were calibrated for energy by comparison with the absorption

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edge positions in a set of topographs in which the specimen was rotated by 0.025° steps between each topograph. A composite photograph of the successive topographs is shown in Fig.7. This provides an internal calibration that eliminates uncertainties due to curvature of the specimen, though it would not be necessary on a truly flat specimen. The energies corresponding to minima in the EXAFS spectrum are shown in Table I for the present results and the standard spectrum. The agreement leaves no doubt that this white-beam method measures true EXAFS data, simultaneously with the topographic image, with an exposure time of 25 seconds in this case.

Discussion

It is clearly necessary to know what is the quality of the EXAFS spectra obtained by this means (the images show normal topographic resolution and contrast). There are several factors to be considered:

1. Dispersion and energy range.

2. Effect of finite source height.

3. Effect of source divergence.

4. Wavelength acceptance of crystal reflection.

5. Spatial resolution of photographic plate.

Let the source height be $\underline{h}$, the source-specimen distance $\underline{a}$, the specimen-detector distance $\underline{b}$ and the Bragg angle θ. ϕ_o and ϕ_h are as usual the angles made by the incident and diffracted beams with the inward-facing surface normals and $\gamma_o = \cos\phi_o$, $\gamma_h = \cos\phi_h$. Examples of the application of the equations will be given for the case corresponding to the experiment reported above: Nb 002 reflection, $\gamma_o = \gamma_h = 1$, d-spacing 1.6503 Å, $\theta = 11.4105°$ at the K absorption edge which is at 0.65298 Å, $\underline{a} = 81$ m, $\underline{b} = 75$ mm.

The position of a point on the image is defined by its perpendicular distance $\underline{x}$ to the absorption edge, with the photographic plate set normal to the diffracted beam. Straightforward geometry gives, assuming for the moment a point source, a dispersion relation:

$$\frac{\delta\lambda}{\lambda} = \frac{\gamma_o}{\gamma_h} \cot\theta \cdot \frac{x}{a} \qquad (1)$$

if $\underline{b}$ is small, otherwise (since the diffracted rays converge from the specimen)

$$\frac{\delta\lambda}{\lambda} = \cot\theta \cdot \frac{x}{a\frac{\gamma_h}{\gamma_o} - b} \qquad (2)$$

For the Nb example this gives a wavelength or energy dispersion of 6.12×10^{-8} per µm or 3.06×10^{-7} per 5 µm digitising element. Over a 10 mm image, the range is thus 6.12×10^{-4}. These figures correspond to 0.0058 eV resolution and 11.6 eV range. This spectral resolution cannot be achieved in practice for various reasons, discussed below, but the range in the Nb sample discussed above was approximately 300 eV over 2 mm (from internal calibration) therefore the specimen was curved with approximately 0.63 m radius of curvature. One purpose of recording the absorption edge position as a function of inclination was to determine this curvature, near a notch in the specimen.

The dispersion is thus adequate for XANES measurements on a flat specimen, but for a full EXAFS spectrum several topographs should be taken at different inclinations. Most SR beam lines are much shorter than 80 m and so greater energy spread would occur.

The finite source height (in the incidence plane) has a great effect on the resolution. Imagine a parallel beam the height of the source fall-

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ing on the specimen. This will be diffracted to a beam the same height (multiplied by the asymmetry factor γ_h/γ_o) and be recorded on the film, blurring spectral data in this region. The minimum useful area on the film is therefore $\underline{h} \gamma_h/\gamma_o = x_{min}$. This can be combined with the dispersion equation (1) to give the minimum spectral resolution

$$\frac{\delta\lambda}{\lambda}\bigg|_{min} = \frac{h \cot \theta}{a} \qquad (3)$$

(with a corresponding equation if (2) is used). For the niobium example with the SRS FWHM value of $\underline{h} = 300$ μm, we obtain for the Nb example

$$\frac{\delta\lambda}{\lambda}\bigg|_{min} = \frac{\delta E}{E}\bigg|_{min} = 1.84 \times 10^{-5} \text{ or } \underline{0.35 \text{ eV}}$$

If now $\underline{x}$ is taken to be $\underline{h} \gamma_h/\gamma_o$ then the apparent source divergence is $2h/a$. For the SRS at $\underline{a} = 81$ m, this results in

$$\frac{\delta\lambda}{\lambda} = \cot \theta \cdot 7.4 \times 10^{-6} \qquad (4)$$

For Nb_{002}, this becomes 3.7×10^{-5}, $\sim \underline{0.7 \text{ eV}}$.

The effect of the wavelength acceptance of the crystal is found from the FWHM of the rocking curve as $\delta\theta$, using $\delta\lambda = \cot\theta\delta\theta$. For an appropriate FWHM ~ 5 arcsec, this gives

$$\delta\lambda = 1.72 \times 10^{-4} \text{ or } \underline{3.25 \text{ eV}}.$$

The effect of the spatial resolution of the plate ≤ 1 μm, is quite negligible on the spectral resolution ($\delta\lambda/\lambda \sim 10^{-7}$), because the intrinsic dispersion is so high.

Combining these three effects (source height, divergence and wavelength spread) by taking the root of the sum of the squares leads to an energy resolution in the Nb case of 1.3×10^{-4} or ~ 2.4 eV. This is perfectly acceptable for the purpose. The dominant factor is the wavelength

acceptance of the crystal; it should be noted that this can easily be decreased by using a weaker reflection.

The signal/noise ratio on the spectra in Figs.5 and 6 is poor and not normally acceptable for a useful EXAFS spectrum: note that the specimen was $\sim 5 \times$ thicker than the ideal. However, only 4 pixels were involved in each smoothing operation, giving 20 μm spatial resolution, whereas as shown above, the minimum useful pixel size is $h\gamma_h/\gamma_o = 300$ μm in this case. Since nuclear emulsion can record up to about 5 photons μm^{-2} at this wavelength, smoothing over a 300 μm range would give a dynamic range of $5 \times 300^2 = 4.5 \times 10^5$ and a corresponding precision of 0.15%. Whilst this is still not as good as the best EXAFS experiments it is acceptable for many purposes. Since the spatial resolution required is so modest, X-ray TV detectors could very probably be used after calibration to collect data to any required precision. Since the TV signal can be directly digitised and used in an image processor[7] to extract the EXAFS information, this could be very convenient.

What then are the applications of this technique? Whilst it is a rapid and convenient way of obtaining EXAFS spectra if good crystals are available they often are not, at least without considerable effort. The interest must lie in the ability to perform chemical and defect crystallography on the same sample. Applications such as structural changes near interfaces with segregation or at decorated dislocations, valence state changes in defect ionic compounds (e.g. iron salts, some of which are important catalysts), structural changes at the onset of chemical decomposition are possible. It is probable that it would not be necessary to scan the specimen in orientation in order to reconstruct the complete spectrum for each pixel on the image. A structural or chemical change at a pixel,

from sufficient volume of the specimen, would result in a distortion of *either the position* or the intensity of the local fringe pattern. This would often provide the clue to anomalous behaviour, which could be followed up with techniques such as microbeam EXAFS over a small, closely defined area, or microbeam trace element analysis, all on the same *apparatus.*

It is also apparent that similar contrast is to be expected in radiographs taken near absorption edges with non-dispersive monochromators such as a single crystal, or the (+,-) channel crystal. With asymmetric-cut beam conditioners, it would be possible to demagnify the source and avoid the limitations of finite source height. With brighter and more intense sources, TV detectors and image processors, dynamic topographic EXAFS should be a real possibility.

Acknowledgements

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Table I. Comparison of X-ray energy at spectral minima in data extracted from the topograph (Fig.3) and from a standard EXAFS spectrum (Fig.6).

FRINGE	FROM TOPOGRAPH keV	FROM SPECTRUM keV
Edge	18.99	18.990
1	19.07	19.074
2	19.13	19.124
3	19.19	19.180
4	19.24	19.252
5	19.29	19.330

Estimated errors are ± 0.01 keV from the topographic data and ± 0.005 keV from the spectral data with the exception of fringe 5 (rather broad) where they are each about ± 0.02. The topographic data were calibrated relative to the edge taken as 18.99 keV.

Figure captions

1. Experimental arrangement for white beam topography. Typical specimen-source distances, _a_, are 20-80 m and specimen-film distances, _b_, 10-100 mm.

2. White radiation topograph of Nb specimen (near perfect but with some elastic bending). 002 reflection, λ = 0.65298 Å at the absorption edge. SRS parameters 2 GeV 86 mA, 25 s exposure on Ilford L4 plate.

3. Digitised and image processed (smoothed, threshold cut and contrast stretch) version of Fig.2. Image area 2.24 × 2.24 mm.

4. Differentiated version of Fig.3.

5. Density traces extracted from Fig.3. (a) along line AA, (b) along line BB. Traces inverted to correspond to normal EXAFS spectrum.

6. EXAFS spectrum of Nb at K edge, measured on rotating anode generator on 25 μm foil: Mo anode, Si(800) curved crystal monochromator. Courtesy P. Georgopoulos, Northwestern Univ., Evanston, Illinois, U.S.A.

7. Composite topograph of area shown in Fig.2, showing successive positions of absorption edge as specimen rotated in 0.025° steps.
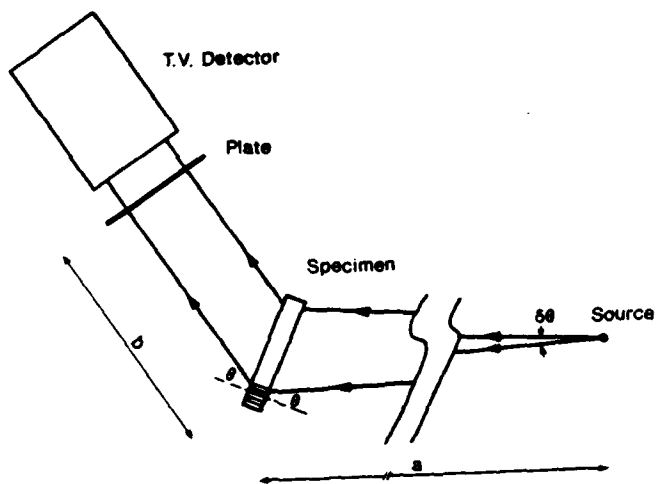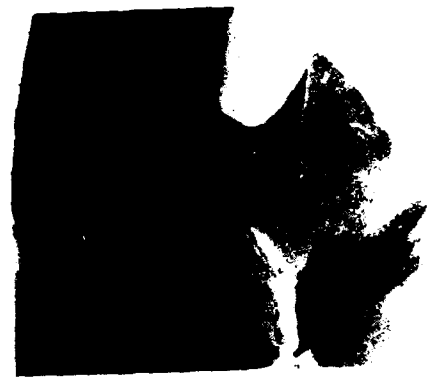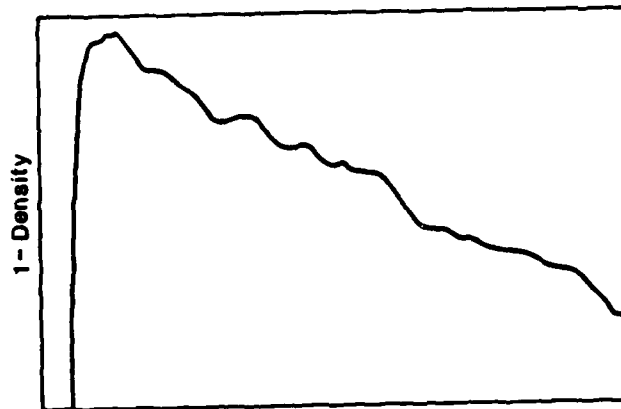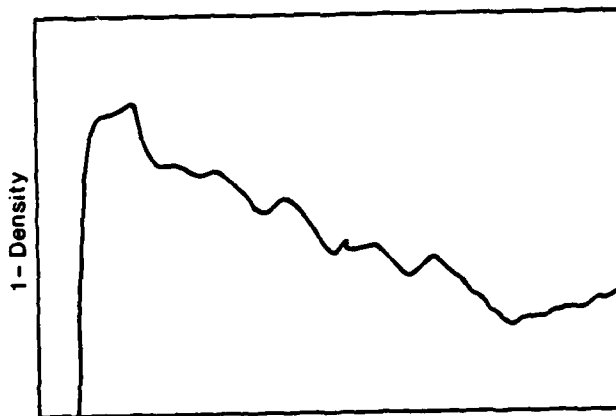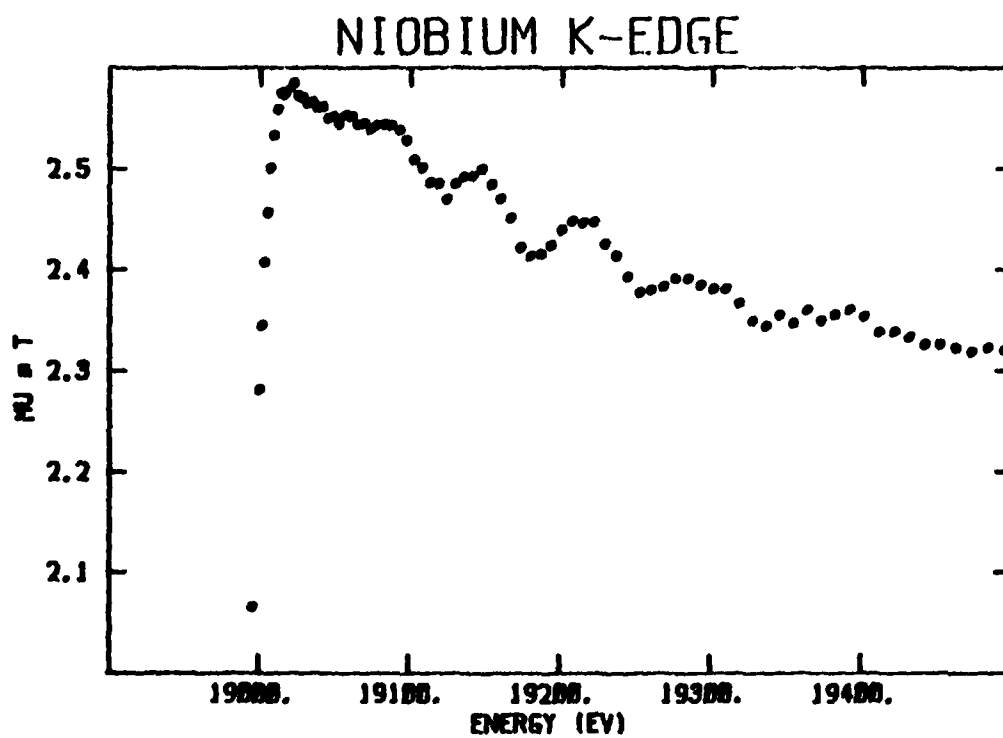
Fig 1

Fig. 2

Fig.3

Fig.4

Distance
(a)

Distance
(b)

Fig. 5

NIOBIUM K-EDGE

Fig.6
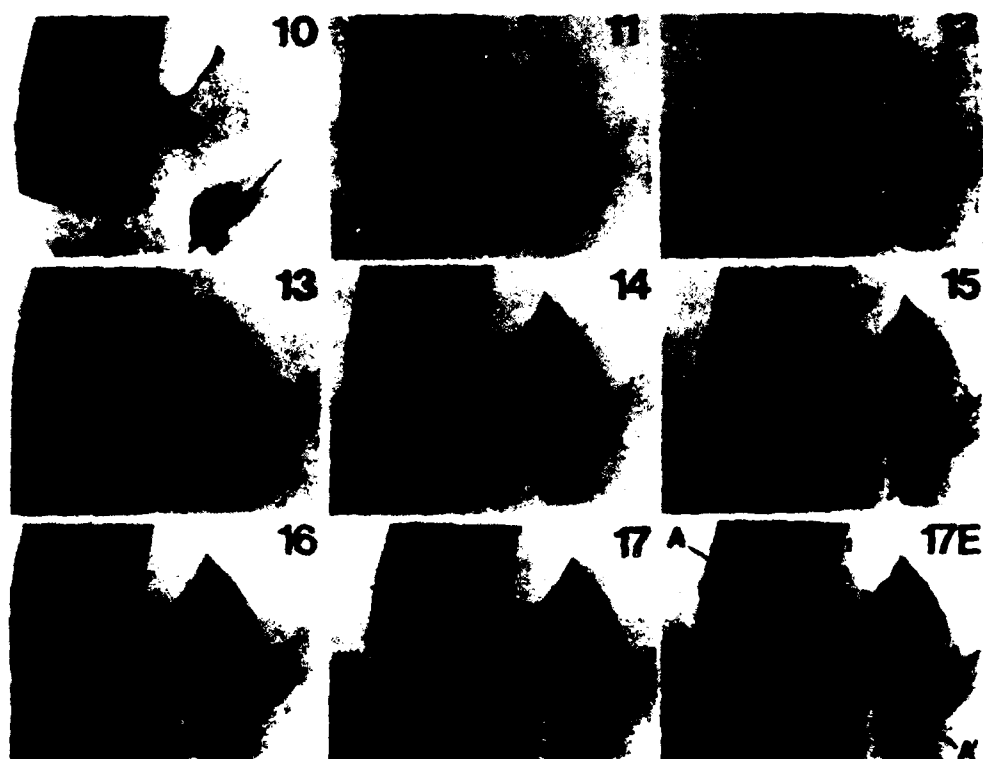
Fig. 7

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